Origin of visible-light activity of N-doped TiO_2 photocatalyst: Behaviors of N and S atoms in a wet N-doping process

Taizo Sano*, Nobuaki Mera, Yusuke Kanai, Chifumi Nishimoto, Sakiko Tsutsui, Tsutomu Hirakawa, Nobuaki Negishi

National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

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ABSTRACT

Behaviors of N and S atoms in formation of N-doped TiO_2 with a wet N-doping process were analyzed to investigate the origin of photocatalytic activity under visible light. In a titanium oxyhydroxide precursor obtained by mixing titanium oxysulfate and ammonia solutions, two types of NH_3 species were formed. One was directly bonded to Ti^{4+} (coordinated NH_3, located at 400.0 eV in X-ray photoelectron spectrum), which was related to photocatalytic activity on NO_x removal under visible light ($\lambda > 405$ nm). The other was NH_3 in $(NH_4)_2SO_4$ (at 401.8 eV), which was unnecessary for producing the activity. During heat-treatment at 400 °C, roughly half amount of the coordinated NH_3 was left behind in TiO_2 without changing the oxidation state of nitrogen, and the other half was released from the solid phase regardless of partial O_2 pressure. A local unusual structure of TiO_2, e.g. crystal defects and distortion, formed by the coordination of NH_3 to Ti^{4+} and/or the release of NH_3 seems to be an origin of the visible-light activity of N-doped TiO_2. A substitutional doping of nitrogen anions (N^{3-}) into TiO_2 was not essential for the activity. The amount of SO_4^{2-} in N-doped TiO_2 was decreased by washing of the precursor or heat-treating the photocatalyst in CO. The activity was significantly improved by decreasing the amount of SO_4^{2-} in N-TiO_2.

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1. Introduction

Titanium dioxide (TiO_2) is the most widely used photocatalyst for air cleaning, water purification, self-cleaning, self-sterilizing, etc. [1–3]. However, the activities of TiO_2 in an indoor environment is often low since UV light, which is essential for activating pure TiO_2, is insufficient. Therefore, many researchers have devoted considerable efforts to develop visible-light responsive photocatalysts. The major part of indoor light is visible light, and therefore, an efficient utilization of visible light will improve the photocatalytic performances. Since TiO_2 has many advantages against other photocatalysts, e.g. high photostability, high resistance for acid and base, low toxicity, large deposit, and cheap price, the modification of TiO_2 is an attractive approach to develop a visible-light responsive photocatalyst.

After the report discussing anion-doping into TiO_2 lattice was published by Asahi et al. [4], the doping of N, S and C into TiO_2 has been widely studied to develop visible-light responsive photocatalyst. Nitrogen-doped TiO_2 (N-TiO_2) was prepared by reduction with gaseous NH_3, sputtering with N_2 molecule, or hydrolysis of titanium salt by ammonia solution. These N-TiO_2 absorbed

visible light with the wavelength below 550 nm, and revealed the photocatalytic activities on oxidation of organic molecule, super-hydrophilicity, antibacterial effect, etc. [4,5]. We also succeeded in preparing a different type of N-doped TiO_2 from titanium-bipyridine complex (TBC) [6]. The newly prepared TiO_2 oxidized NO into NO_3^- under visible light with longer wavelengths ($\lambda < 650$ nm), and the oxidation rate at the wavelengths above 450 nm was more than 10 times as high as that of a conventional N-TiO_2. The co-doping of carbon and nitrogen atoms into the anatase lattice was proposed to explain the expanded visible-light activity. However, the photocatalyst derived from TBC did not degrade organic molecules under humid condition. It was inferred that the oxidation potential of the photocatalyst was too low to oxidize water, and the degradation did not take place at a site where a water molecule was adsorbed once [7]. Umebayashi et al. reported the formation of S-doped TiO_2 by an oxidation of titanium disulfide (TiS_2), in which a S anion occupied an O-atom site in TiO_2 lattice [8]. Also, doping of S cation by the calcination of thiourea with TiO_2 powder was reported [9]. In both the reports, the visible-light activity of S-doped TiO_2 was confirmed.

One of the most important preparation methods of anion-doped TiO_2 is a calcination (at ca. 400 °C) of hydroxide (or oxyhydroxide) precursor obtained by hydrolysis of titanium salt by an ammonia solution (wet N-doping process) [10]. Titanium sulfate or titanium oxysulfate is often used as a titanium salt because of their low

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* Corresponding author. Tel.: +81 29 861 8451; fax: +81 29 861 8866.
E-mail address: sano-t@aist.go.jp (T. Sano).

material costs and high stabilities. By the calcination and heat-treatment of the hydroxide precursor, parts of N and S atoms of ammonia and sulfate may remain in the product (N-TiO$_2$), and this would modify the photocatalytic activity of TiO$_2$ under visible light.

However, the origin of the visible-light activity derived by wet N-doping process is not well-understood. Although β-substituted N is inferred as the origin of the visible-light activity for N-TiO$_2$ obtained by reduction with gaseous NH$_3$ at above 600 °C or sputtering [4,11], the N-TiO$_2$ produced by wet N-doping cannot contain β-substituted N. On the other hand, Ihara et al. attributed the visible-light activity to the formation of oxygen-deficient sites in the grain boundary of polycrystalline TiO$_2$ [10].

In this paper, we focused on the behaviors of NH$_3$ species and SO$_4{}^{2-}$ ion in a wet N-doping process, and discussed the origin of visible-light activity of N-TiO$_2$. We analyzed the states and the concentrations of S and N ions in hydroxide precursors and N-TiO$_2$, and evaluated their effect on the photocatalytic activity under visible light.

2. Experimental

2.1. Preparation of photocatalysts

The N-doped TiO$_2$ was prepared by a wet N-doping method. An ammonia solution (4.6 mol/dm^3) was added dropwise into a TiOSO$_4$ solution (0.60 mol/dm^3) until the pH of the solution became 7.0 while mixing vigorously and cooling with an ice bath. The produced white precipitate of the titanium oxyhydroxide was collected by the aid of centrifugation. The precipitate was divided into 7 centrifugation tubes. 35 ml of water was added into each tube, and the tubes were shaken for 30 min. The precipitate was separated from the washings by centrifugation. This washing process was repeatedly performed for 0–6 times, and the 7 precursors with different ionic contents were obtained.

The contents of ammoniac nitrogen (NH$_3$ species) in the precursors were analyzed with ammonium ion analyzer (Kasahara Rika Kogyo, NH$_4$-1F) after dissolving 0.1 g of the precipitates in a H$_2$SO$_4$ solution (1.8 mol/dm^3). The contents of SO$_4{}^{2-}$ ion were analyzed with ion chromatography (Tosoh, IC-2001) after dissolving the precursor in a conc. H$_2$O$_2$ solution containing 0.5 mol/dm^3 of NaOH. The contents of Ti^{4+} ion were calculated from gravimetric data.

Each of the precursors was placed in a quartz tube (diameter 25 mm), and was calcined in air at 300 °C for 1 h. The calcined precursor was ground in an agate mortar, and then was heat-treated in air, Ar or CO gas stream (0.20 dm^3/min) at 400 °C for 1 h. Thus obtained N-TiO$_2$ photocatalysts were named as PC(n, A), where n indicates the number of washing steps performed for the precursor, and A indicates the atmosphere used for the heat-treatment at 400 °C, respectively.

The photocatalysts were analyzed with UV–vis diffuse reflectance spectroscopy (Shimazu, UV-3600), X-ray diffractometry (XRD) with Cu-Kα radiation (Rigaku, model RU-300), and X-ray photoelectron spectroscopy (XPS) with Al-Kα radiation (Fisons instruments, Escalab220i-XL). The binding energy of XPS was calibrated using C1s peak at 248.8 eV as an internal standard. The specific surface areas were determined by BET method with N$_2$ adsorption at 77 K (Quantachrome, AS-1).

2.2. Photocatalytic activity

The photocatalytic activity of N-TiO$_2$ was analyzed with NO$_x$ removal (i.e. oxidation of NO into NO$_3{}^-$) under visible light. A flow type reactor (Fig. 1) was used because precise controls of NO concentration (lower than 2 ppmv) and humidity were possible [12,13]. A 100 mg of N-TiO$_2$ suspended in 2 ml of distilled
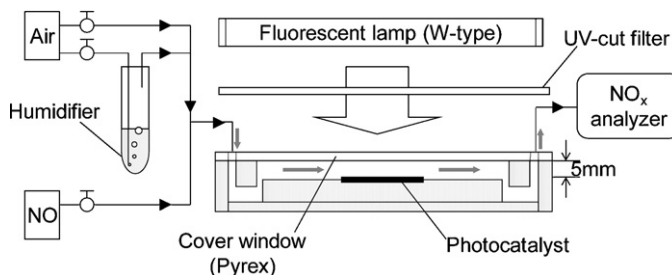

Fig. 1. Flow type reactor for analysis of photocatalytic NO$_x$ removal.

water was dispersed on a glass plate (5 cm × 10 cm), and was dried at 50 °C for 1 day. The plate with photocatalyst was placed in the reactor covered with a Pyrex glass window. The test gas containing NO (ca. 1.6 ppmv, humidity 50% at 25 °C) was passed through the space between the photocatalyst and the window (5.0 mm thick air layer) at the flow rate of 1.0 dm^3/min. The photocatalyst was irradiated with visible-light (6000 lx) from W-type fluorescent lamps (Toshiba, FL-10W). The UV light contained was removed with UV-cut filter (Nitto jushi kogyo Co., N-113 and N-169). The cut positions of N-113 and N-169 were 418 nm and 394 nm, respectively. The transmittance of N-113 below 405 nm was less than 0.3%, and UV light was considerably removed by the filter. The spectrum of the W-type fluorescent lamp and the transmittance spectra of the UV-cut filters were shown in Fig. S1. The photon flux irradiated to the photocatalyst was shown in Fig. S2. The number of photon with wavelength shorter than 500 nm was 3.0 mmol/h (with N-169 filter) and 2.6 mmol/h (with N-113). The concentrations of NO and NO$_2$ were analyzed by a chemiluminescence NO$_x$ detector (Monitor Lab., ML-8940A). The NO$_x$ removal ratio (%) was defined as [amount of NO$_x$ removed]/[amount of NO flowed] × 100 during 1-h illumination, where [amount of NO$_x$ removed] = [amount of NO removed] − [amount of NO$_2$ formed] [6].

3. Results and discussion

3.1. Screening of titanium hydroxide precursor

The screening of chemical reagents for the preparation of titanium oxyhydroxide precursor was performed. TiCl$_4$ or TiOSO$_4$ was used for Ti^{4+} source, and NH$_3$ solution or NaOH for OH$^-$ source. The precursor prepared by mixing aqueous solutions of Ti^{4+} and OH$^-$ sources was calcined in air at 300 °C for 1 h, and then was heat-treated at 400 °C in air for 1 h. The UV–vis spectra of the products were measured by diffuse reflection method (Fig. S3). The products derived from NH$_3$ solution absorbed visible light at around 400–550 nm, while the product derived from NaOH solution did not absorb visible light. The spectrum of the product derived from TiCl$_4$ was similar to that derived from TiOSO$_4$ in the visible-light region These results suggest that NH$_3$ was indispensable for the visible-light absorption while Na$^+$, SO$_4{}^{2-}$ and Cl$^-$ ions were not related to the visible-light absorption. In the following experiment, the precursors obtained by mixing TiOSO$_4$ and NH$_3$ were used.

3.2. Analysis of concentration of NH$_3$ species and SO$_4{}^{2-}$ in precursor

The concentrations of NH$_3$ species and SO$_4{}^{2-}$ ions in the oxyhydroxide precursor were analyzed. The concentrations were plotted against the number of washing steps of the precursor (Fig. 2). The concentration of SO$_4{}^{2-}$ ion simply decreased. On the other hand, the concentration of NH$_3$ species decreased until washing steps of 3, and then the decrease became negligible. Here, we supposed that the precursor derived from NH$_3$ and TiOSO$_4$ solutions
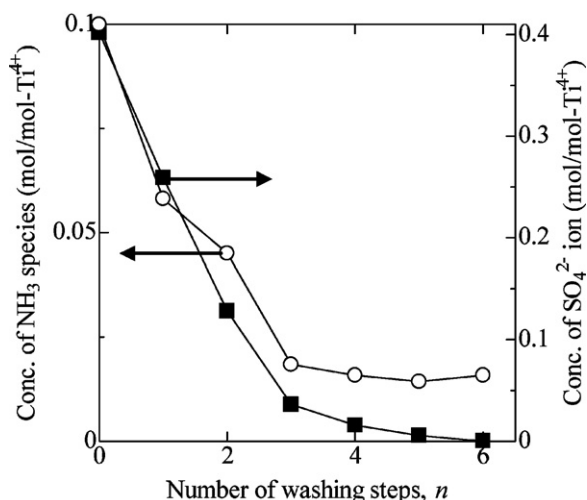
Fig. 2. Change in concentrations of NH_3 species and SO_4^{2-} ions in the precursor with number of washing steps.

Fig. 4. Time-course of the concentrations of NO, NO_2 and NO_x in the presence of PC(6, Ar) under visible light ($\lambda > 380$ nm).

contains two types of NH_3 species at least; one is a NH_3 species that is easily removed by water, and the other one is a NH_3 species that is tightly fixed in the precursor. The concentrations of NH_3, which may include NH_4^+, and SO_4^{2-} in the precursor washed 5 times were 0.016 mol/mol-Ti^{4+} and 0.0054 mol/mol-Ti^{4+}, respectively.

The precursors were dried at 80 °C, and were analyzed by XRD (Fig. 3). In the XRD spectra of precursors with washing steps of 0–2, the peaks of $(NH_4)_2SO_4$ were observed along with the peaks of anatase type TiO_2. The peaks of $(NH_4)_2SO_4$ gradually decreased with washing, and no peaks of $(NH_4)_2SO_4$ were observed in the spectra of the precursor washed more than 3 times. The decrease in the concentration of NH_3 species in Fig. 2 was attributed to the removal of $(NH_4)_2SO_4$.

The dried precursors were calcined at 300 °C for 1 h in air, and then were heat-treated at 400 °C for 1 h in air, Ar or CO. All the photocatalyst samples obtained showed only the peaks of anatase type TiO_2 in the XRD spectra (Fig. S4). The crystallite sizes and the specific surface areas were listed in Table S1. The crystallite sizes
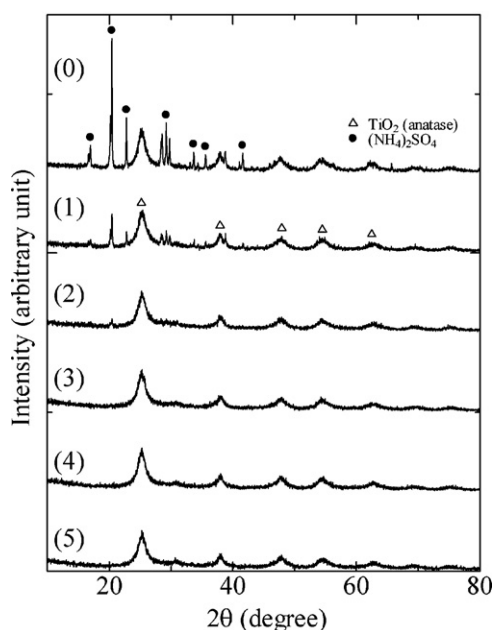

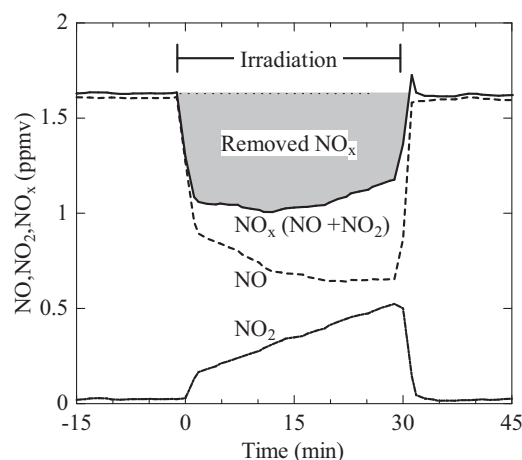**Fig. 3.** XRD spectra of precursors dried at 80 °C. Number in parenthesis indicates the number of washing steps.

of anatase phase of all the samples were between 4.6 and 7.2 nm. For the photocatalyst obtained from the precursors with washing steps of 3–5, the specific surface areas were from 134 to 186 m²/g. A photocatalytic reaction rate often depends on the specific surface area (and/or the crystallite size). However, in this case, the differences in the surface areas were small enough, compared with the difference in photocatalytic NO_x removal activities discussed in the next section.

3.3. NO_x removal activity

A typical profile of NO_x removal test was shown in Fig. 4. As soon as visible-light irradiation ($\lambda > 380$ nm) onto the N-TiO_2 photocatalyst (PC(6, Ar)) started, the NO concentration decreased and the NO_2 concentration increased. After the irradiation was stopped, the concentrations of NO and NO_2 recovered to the initial concentrations. During the irradiation, the total NO_x concentration, which is the sum of NO and NO_2 concentrations, was lower than the initial NO_x concentration. These results indicate that the changes in the NO and NO_2 concentrations are initiated by visible-light illumination, and that part of NO was oxidized into NO_3^- which was adsorbed on the surface of photocatalyst [3,6].

The NO_x removal activity of the prepared N-TiO_2 (PC(6, CO)) was compared with those of conventional TiO_2 (Degussa P25 and Ishihara ST-01) (Fig. 5). When the W-type fluorescent lamp was used without the UV-cut filters, ST-01 revealed the highest NO_x removal ratio. This indicates that the light from fluorescent lamp contains UV light that excites conventional TiO_2 to oxidize NO molecule. Applications of the UV-cut filters significantly decreased the NO_x removal ratios of ST-01 and P25. When N-113 filter was applied and only light with wavelength longer than 405 nm was irradiated, N-TiO_2 clearly revealed the highest NO_x removal ratio. These results indicate that the N-TiO_2 utilizes a longer wavelength range of visible light that is not utilized by conventional TiO_2, and that the apparent quantum efficiency of N-TiO_2 under visible light is higher than those of the conventional TiO_2. In the following experiment, N-113 filter was applied to irradiate visible light that cannot efficiently excite the conventional TiO_2.

The relation between the photocatalytic activity and the concentration of NH_3 species or SO_4^{2-} in the precursor was analyzed. Fig. 6 shows the plot of NO_x removal ratio against the number of washing steps. The NO_x removal ratios of PC(0–3, air) and PC(0–3, Ar) were almost zero. The removal ratio increased drastically with number of washing steps, n, when n was larger than 3. These result suggests that the visible-light activity of N-TiO_2 is due to
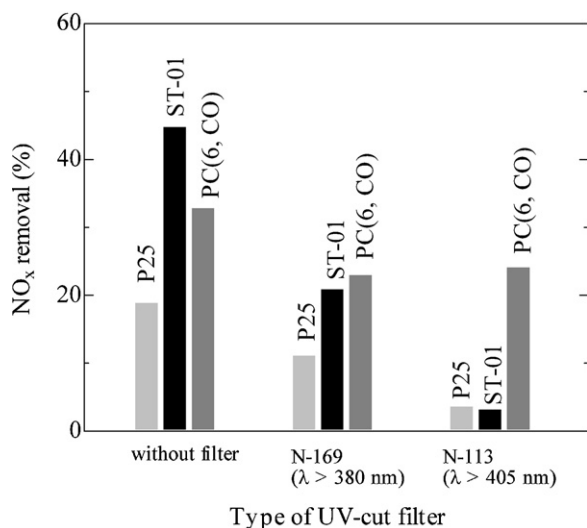
Fig. 5. NO_x removal ratios of PC(6, CO), P25 and ST-01 under different light conditions.
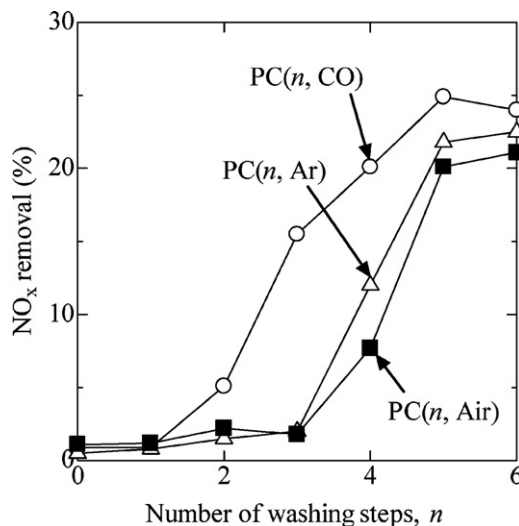

Fig. 6. Improvement of photocatalytic NO_x removal ratio under visible light ($\lambda > 405$ nm) with increasing number of washing steps. UV-cut filter (N-113) was applied.

the fixed NH_3 species remained after the washings, since most of the $(NH_4)_2SO_4$ in the precursor was removed by washing 3 times. However, the NH_3 concentration was not responsible for the drastic increase ($n > 3$) in the NO_x removal ratio since, as shown in Fig. 2, the NH_3 concentration in the precursor was approximately constant (0.016 mol/mol-Ti at $n > 2$). Also, the difference in the specific surface areas of PC(2, air or Ar) and PC(3–6, air or Ar) were smaller than 20% (Table S1). It is inferred that the decrease in SO_4^{2-} concentration drastically improved the photocatalytic activity of N-TiO_2 by eliminating a recombination center.

The heat-treatment in CO also improved the photocatalytic activity of N-TiO_2. The NO_x removal ratio of PC(n, CO) was significantly larger than those of PC(n, Ar) and PC(n, Air) when n was 2–5. Especially, the improvement effect was large when n was 2 or 3. The samples treated in CO showed the higher NO_x removal ratio (>15%), while the samples heat-treated in air or Ar showed the smaller values (<3%). The role of CO treatment in the improvement of photocatalytic activity is discussed in Section 3.5.

3.4. Change in XPS spectra and UV–vis spectra by washing of precursor

The chemical states of constituent elements in the precursors dried at 80 °C were analyzed by XPS. The Ti2p and O1s spectra of the precursors were almost the same as that of the conventional TiO_2. The precursors contained two types of N species, which were responsible for the peak at 400.0 ± 0.1 eV and 401.8 eV (Fig. 7(a)). Since ammonia is hardly decomposed at 80 °C in air, the peaks must be due to NH_3 or NH_4^+. The peak area of 401.8 eV was decreased by washing with water. This result indicates that the N species related to 401.8 eV is contained in the soluble salt, $(NH_4)_2SO_4$. The peak position was not far from that of nitrogen atom in a similar salt, NH_4Cl (401.7 eV) [14]. The NH_3 species at 400.0 eV seemed to be held in the precursor strongly, since the peak area of 400.0 eV was not decreased by washing. In a literature [15], N1s peak of NH_3 coordinated to Fe located at 399.8 eV. Therefore, the N1s peak at 400.0 was attributed to NH_3 coordinated to Ti^{4+} ion. In the chemical analysis of the concentration of NH_3 species in the precursor (Fig. 2), the concentration did not become less than 0.016 mol/mol-TiO_2 even when the precursor was repeatedly washed. It is inferred that the lowest concentration of NH_3 species corresponds to the concentration of NH_3 coordinated to Ti^{4+} that was not released by washing.

The N1s peak at 400 eV was observed even after the heat-treatment at 400 °C, regardless of washing steps or heat-treatment atmosphere (Fig. 8). No peak of β-substituted N (396 eV) was observed. It is suggested that the coordinated NH_3 in the precursor was incorporated into TiO_2 lattice without changing the oxidation state of nitrogen by the heat-treatment at 400 °C. Thus, a substitutional doping of nitrogen anion (N^{3-}) into TiO_2 [4] was not essential for the visible-light activity. The peak area was smaller than that observed before the heat-treatment. It is considered that part of NH_3 coordinated to the Ti^{4+} in the precursor stayed in the photocatalyst and the other part of NH_3 released from the solid phase during the heat-treatment. The concentrations of NH_3 in the photocatalysts were calculated from the peak areas and are listed in Table 1. The amounts of NH_3 released from the precursors were 43–74% of the coordinated NH_3. These values suggest two possibilities of origin of the visible-light activity: one is the survived NH_3 coordinated to Ti^{4+}, and the other is a local defect structure formed in the NH_3 release. In both the cases, the coordinated NH_3 should have important roles.

However, the visible-light activity of N-TiO_2 has been attributed to other kinds of nitrogen species by many authors. Diwald et al. attributed the visible-light activity to a form of N bound to hydrogen (NH_x), whose XPS peak is located at 399.6 eV [16]. This attribution is consistent with the result of this paper. Sato et al. reported the oxidation state of doped N was found close to that of NO [5]. Asahi et al. reported β-substituted N, which has XPS signal at 396 eV, is responsible for the visible-light sensitization [4]. The presence of β-substituted N was supported by a several authors, while low photocatalytic activity of β-substituted N was claimed [17–19]. A recent study using density functional theory (DFT) suggested that a complex defect of nitrogen anion at an oxygen site (N_O^{1-}) with a titanium ion at an interstitial site (Ti_i) provides visible-light absorption [20]. Wang et al. and Bellardita et al. attributed the visible-light sensitization to oxynitride (Ti—N—O, N—Ti—O) at 399–401 eV [19,21]. Furthermore, the photocatalysts obtained by oxidation of titanium nitride (TiN) or titanium complex with nitrogen-containing ligand revealed photocatalytic activity under visible light [6,22], although those photocatalysts cannot contain NH_3 species. Apparently, therefore, the presence of NH_3 coordinated to Ti^{4+} is not essential to generate visible-light activity of N-TiO_2.

Table 1
Concentrations of N or S to Ti atom in photocatalyst calculated from peak area of XPS spectra.

Sample name	Number of washing steps	Heat-treatment atmosphere[a]	Concentration (mol%)		
			$N(NH_3-Ti^{4+})/Ti$	$N(NH_4^+-SO_4^{2-})/Ti$	S/Ti
Precursor 2	2	–	5.0	8.9	7.0
PC(2, air)	2	Air	2.9	4.8	16.1
PC(2, Ar)	2	Ar	2.1	2.6	14.6
PC(2, CO)	2	CO	2.0	0.5	3.4
Precursor 5	5	–	4.3	3.0	1.5
PC(5, air)	5	Air	1.6	0.2	nd
PC(5, Ar)	5	Ar	2.1	0.1	nd
PC(5, CO)	5	CO	1.9	0.1	nd

nd: not detected.

[a] Heat-treatment was performed at 400 °C for 1 h.

Although many kinds of nitrogen species have been doped to TiO_2, the absorption spectra of the derived TiO_2 are similar to each other. This suggests that the orbitals of doped nitrogen are not responsible for modifying the electron structure of TiO_2 but some local unusual structures, such as crystal defects or distortion, formed during the N-doping process generate the visible-light activity. A similar discussion was thoroughly made by Serpone [23]. He claimed that the absorption features displayed by TiO_2 specimens in the visible spectral region are likely the result of formations of oxygen vacancies and color centers (e.g. F, F^+, F^{++} and Ti^{3+}) originated in the reduction of TiO_2. Also, Ihara et al. [10] prepared TiO_2 with oxygen deficient stoichiometry from $Ti(SO_4)_2$ and NH_3 solutions, and concluded that the oxygen-deficient sites formed in the grain boundaries were responsible for the visible-light activity, while the presence of nitrogen only inhibited the reoxidation of oxygen-deficient sites.

Both of oxygen vacancy (V_O) and interstitial cation (Ti_i in case of TiO_2), which are typical defects formed in partially reduced metal oxides (i.e. oxygen deficient stoichiometry), possibly create new bands in the band gap, although it is unclear whether the presence of those defects directly result in a visible-light activity. According to the DFT calculation by Na-Phattalung et al., V_O is more stable thermodynamically than Ti_i in the anatase TiO_2 [24]. Experimentally, both of V_O and Ti_i that were related to the optical transition between 425 and 620 nm were observed [23,25–29]. Recently, Chen et al. reported a heavily hydrogenated TiO_2 that split water photocatalytically under wide range of visible-light [30]. Their DFT calculations showed that the distorted crystal of hydrogenated TiO_2 induces the visible-light activity and that V_O, Ti_i and interstitial hydrogen atoms without crystal distortion did not induce any visible-light absorption.

In this paper, the residual of NH_3 coordinated to Ti^{4+} and the release of NH_3, which possibly formed the crystal defects and the distortion, were observed. Since distortion and small amounts of crystal defects in TiO_2 nanoparticles are scarcely able to be quantified experimentally, the DFT calculation concerning the presence of coordinated NH_3 would help us to understand the formations of defects and distortion by the NH_3 in the future.

In the S2p region of XPS spectrum of the precursor washed twice, the peak of SO_4^{2-} was observed (Fig. 7(b)). The peak area decreased
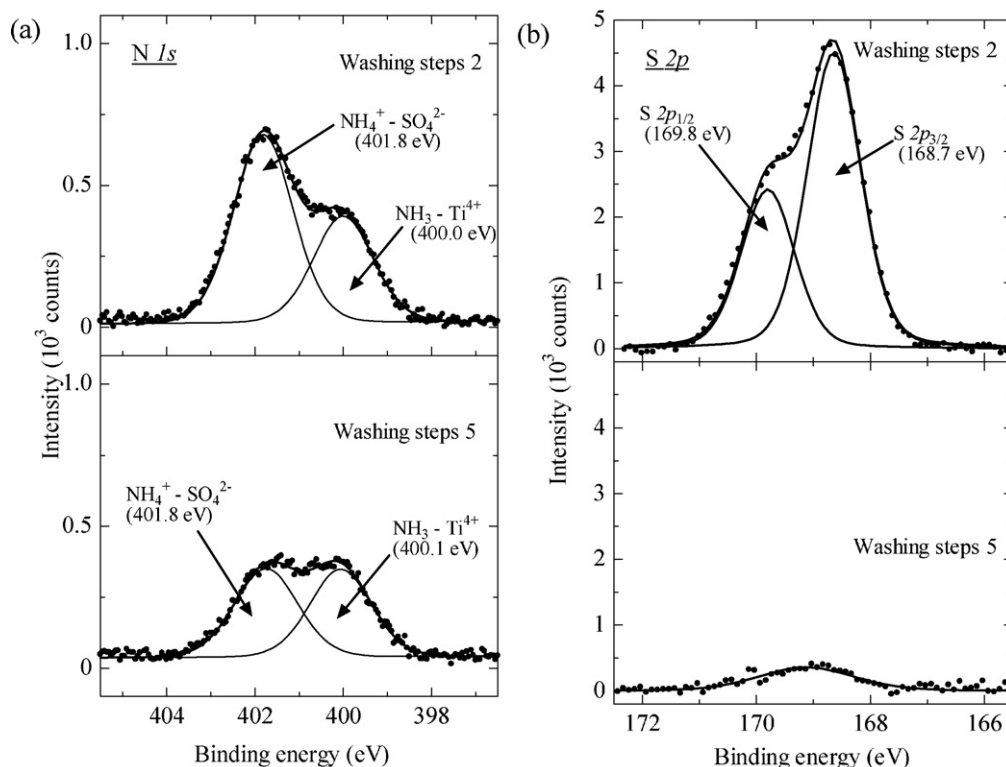

Fig. 7. N1s (a) and S2p (b) XPS spectra of the dried precursors. Spectra of the precursors after washing steps 2 and 5 were compared.
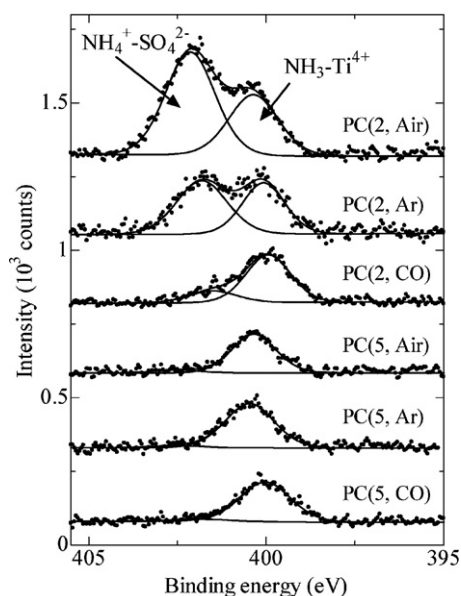
Fig. 8. $N1s$ XPS spectra of $N-TiO_2$ heat-treated at 400 °C in different atmospheres. Intensity was normalized with a peak area of $Ti2p_{3/2}$.

with the number of washing steps. This indicates that the SO_4^{2-} is removed by washing, and that the SO_4^{2-} is not responsible for the visible-light activity.

The UV–vis spectra of the $N-TiO_2$ samples with different number of washing steps were compared (Fig. S5). The visible-light absorbance between 400 and 500 nm was similar to each other, and significant difference was not observed. This suggests that the concentration of NH_3 species that is responsible for the visible-light absorption of $N-TiO_2$ is constant regardless of the number of washing steps.

3.5. Effect of CO treatment

The $N-TiO_2$ obtained by the heat-treatment in CO showed higher NO_x removal ratio than the other photocatalysts (Fig. 6). Here, the role of the CO treatment on the photocatalytic activity was analyzed. Fig. 9 shows the change in the XPS spectrum in the $S2p$ region with the heat-treatment in CO. Before the CO treatment, the peak of SO_4^{2-} was observed in the precursor that was washed twice. After
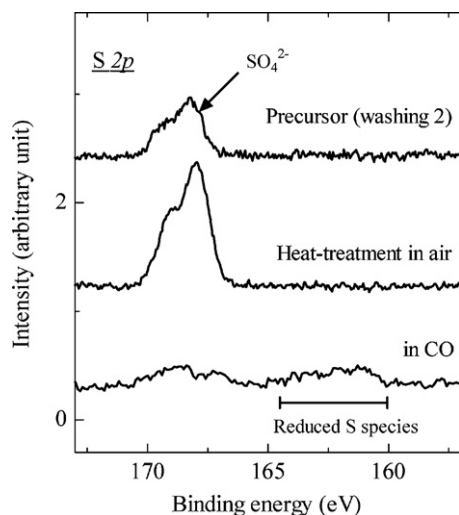

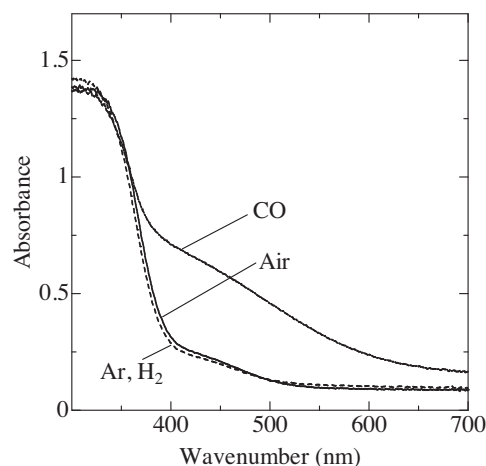**Fig. 9.** Change in XPS spectrum of $S2p$ region with heat-treatment in CO at 400 °C.

Fig. 10. UV–vis diffuse reflectance spectra of $N-TiO_2$ samples obtained by heat-treatment in CO, Air, Ar, and H_2 gas stream at 400 °C. The number of washing steps of the precursor was 2. The spectrum for H_2 was omitted since it is quite similar to that for Ar.

the CO treatment, the peak of SO_4^{2-} became smaller, and the new peak of reduced S species was observed at 160–164 eV. This indicates that the SO_4^{2-} ion in the precursor reacted with CO to form reduced sulfur species, such as S and H_2S, and that the reduced sulfur species were removed from the photocatalyst or adsorbed on the surface. By the heat-treatment in air, the peak area of SO_4^{2-} was not decreased. As shown in Fig. 6, the NO_x removal activities of PC(2–5, CO) was significantly higher than that of PC(2–5, air) or PC(2–5, Ar). These results suggest that the improvement of activity by CO is due to the decrease in the amount of SO_4^{2-} ion that provides recombination center.

The UV–vis diffuse reflectance spectra of the $N-TiO_2$ samples obtained by the heat-treatment (400 °C) in a different atmosphere (CO, air, Ar, or H_2) were compared (Fig. 10). All the samples absorbed visible light with the wavelength between 400 and 500 nm. It is confirmed that the coordinated NH_3 in the $N-TiO_2$ is not completely removed even when the heat-treatment is performed in the presence of oxygen. Only the sample heat-treated in CO showed stronger absorption in the wide range of visible light (400–600 nm). CO gas has stronger reducing power than H_2 gas, and the reduction of SO_4^{2-} in the precursor by CO treatment was confirmed by XPS. The strong visible-light absorption can be attributed to a reduced form of titanium ion (Ti^{3+}), reduced sulfur compounds, and/or carbon formed by disproportionation of CO. Unfortunately, it is inferred that the strong absorption did not improve the photocatalytic activity under visible light since the NO_x removal ratio of PC(5–6, CO) was only slightly higher than that of PC(6, Ar).

4. Conclusions

In the titanium oxyhydroxide precursor obtained by mixing titanium oxysulfate and ammonia solutions, NH_3 coordinated to Ti^{4+} (400.0 eV in XPS) and NH_4^+ in $(NH_4)_2SO_4$ (401.9 eV) were present. The visible-light activity of $N-TiO_2$ was related to the coordinated NH_3. A substitutional doping of nitrogen anion (N^{3-}) into TiO_2 was not essential for the visible-light activity. Part of the coordinated NH_3 (43–74%) was released from the precursor, and the other part of NH_3 stayed in the $N-TiO_2$ during the heat-treatment. Since $N-TiO_2$ without coordinated NH_3 was often reported to be activated with visible light, it is inferred that local unusual structures, e.g. crystal defects and distortion, caused by the coordination of NH_3 to Ti^{4+} and/or the release of NH_3 were responsible for the visible-light activity of $N-TiO_2$. Although it is hard to determine the contribution of the crystal defects and distortion to the activity, the observation

of the release of coordinated NH_3 may support the formations of these unusual structures. Also, it is found that the activity was significantly improved by removing SO_4^{2-} from the precursor. The amount of SO_4^{2-} in N-doped TiO_2 was decreased by washing of the precursor or heat-treating the photocatalyst in CO. In the design of a visible-light responsive photocatalyst, preparation of titanium hydroxide precursor with high concentration of the coordinated NH_3 and low concentration of SO_4^{2-} is important.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.06.034.

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